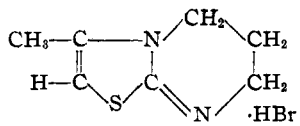

In a 500-cc. flask, 22.4 g. (0.2 mole) of 2-amino-4-methylthiazole,[1] 40.4 g. (0.2 mole) of trimethylene dibromide (Dow), and 60 cc. of absolute ethanol were mixed and the resultant solution was refluxed for four and one-half hours during which time hydrogen bromide was evolved. Upon cooling, 52.5 g. of white crystals melting at 160–191° precipitated. Three recrystallizations from methanol yielded the hydrobromide melting at 235.5–237° (uncor.). The free base was found to be an oil and did not form a picrate.

*Anal.* Calcd. for $C_7H_{11}N_2BrS$: N, 11.9; ionizable Br, 34.0. Found: N, 11.9; ionizable Br (by Volhard), 33.9.

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(1) Bayers and Dickey, *Org. Syn.*, **19**, 10 (1939).

# COMMUNICATION TO THE EDITOR

## CONVERSION OF GLOBULAR TO ORIENTED FIBROUS PROTEINS. I. BY HEAT AND MECHANICAL WORKING

*Sir:*

By a simple process we have converted a number of globular proteins to the fibrous form characterized by the diffraction pattern of β-keratin. In its essence the process involves heating the protein with water, followed by mechanical treatment, such as stretching in cold or hot water or water vapor, to extend and orient the peptide chains. Among the proteins which have thus given β-keratin patterns are casein, β-lactoglobulin, hemoglobin, ovalbumin, edestin, zein, and peanut and soybean proteins. A high degree of double orientation has been achieved in an ovalbumin preparation.

In the initial heating of protein and water, partial crystallization of the protein occurs as evidenced by the change in the diffraction pattern, diffuse rings becoming sharp and the number of rings increasing. At the same time solubility decreases and tenacity increases. After heating, application of high shear stress by extrusion or stretching produces ultimately the parallelism of extended peptide chains which gives rise to the β-keratin pattern.[1]

The best patterns have been obtained from β-lactoglobulin and ovalbumin. Data on these proteins are summarized in Table I, together with indices and corresponding data on β-keratin of stretched wool and hair quoted by Clark.[2]

With the exception of the natural fibrous proteins, β-keratin patterns have been obtained previously only from edestin[3] and ovalbumin,[4,5] using denaturing reagents such as calcium chloride or detergents. From a stretched film of heat-denatured egg white, however, Astbury, Dickinson, and Bailey[3] obtained a different pattern, the 4.7 Å. (backbone) spacing occurring on the meridian and the 9.7 Å. (side chain) spacing on the equator, while for β-keratin both occur on the equator. We have obtained this egg-white pattern from such proteins as casein, peanut protein, hemoglobin, zein, edestin, and ovalbumin. Our experience with these proteins has shown that the structure giving the egg-white pattern can be converted into the β-keratin structure by further mechanical working.

TABLE I

| Indices | Observed spacing and intensity, Å. Lactoglobulin | | Ovalbumin | | β-Keratin | |
|---|---|---|---|---|---|---|
| 001 | 9.7 | S | 9.8 | S | 9.7 | S |
| 200 | 4.68 | S+ | 4.65 | S+ | 4.65 | VS |
| 111 | 4.7 | M | 4.7 | M | 4.7 | M |
| 210 | 3.72 | M | 3.75 | M | 3.75 | S |
| 410 | ... | | 2.2 | W− | 2.2 | W |
| 020 | 3.26 | M | 3.33 | M | 3.33 | S |
| 220 | 2.71 | W | 2.75 | W | 2.7 | W |
| 030 | 2.16 | W | 2.18 | W | 2.2 | W |
| 230 | 2.03 | W+ | 2.03 | W+ | 2.0 | W |

Our results demonstrate that the conversion of globular to oriented fibrous proteins may be expected to be generally practicable. Tensile measurements have shown that the strength of casein, lactoglobulin, and ovalbumin filaments is greatly increased by conversion of the protein to the oriented fibrous form. It seems reasonable that an extension of this work may lead to significantly improved protein plastics, films, and adhesives.

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(1) Addition of other reagents, for example ethanol, to some proteins obviates the necessity of heating.

(2) G. L. Clark, "Applied X-Rays," 3d ed., McGraw-Hill Book Co., New York, N. Y., 1940, p. 648.

(3) Astbury, Dickinson, and Bailey, *Biochem. J.*, **29**, 2351 (1935).

(4) Lundgren and O'Connell, *Ind. Eng. Chem.*, in press.

(5) Palmer and Galvin, THIS JOURNAL, **65**, 2187 (1943).